Available online at www.sciencedirect.com

ScienceDirect

Procedia Engineering 10 (2011) 728–733

Engineering Procedia

ICM11

Fabrication of Ni, Pt, Pt/Ni Nano Powders using Wire Explosion Process and Characterization

Taek-Kyun Jung[a,*], Dong-Woo Joh[a], Hyo-Soo Lee[a], Min-Ha Lee[a]

[a]*Korea Institute of Industrial Technology, 7-47 Songdo-dong, Yeonsu-gu, Incheon 406-840, Republic of Korea*

Abstract

Spherical typed Pt, Ni and Pt/Ni nanoparticles less than 50 nm in particle size were successfully obtained by pulsed wire explosion in D.I. water. The Pt nanoparticles exhibited high purity, but the Ni nanoparticles exhibited a partial and very thin oxide layer. It was confirmed that the obtained Pt/Ni nanoparticles consisted of Pt and Ni nanoparticles as well as PtNi composite nanoparticles of solid solution type.

Keywords: Pulsed wire explosion ; Pt ; Ni ; Pt/Ni ; nanoparticles ; pulsed wire explosion ; TEM

1. Introduction

Recently, metallic nanoparticles or composite nanoparticles are used for various industrial fields such as mechanical and chemical engineering including catalyst and bio-sensor. Basically, a reduction in powder size to the nanometer scale results in various interesting properties such as the lower melting point compared to the bulk, the lower sintering temperature, the quantum size effects and the high surface area, etc. Fabrication methods for the product of metallic nanoparticles have been developed in the last years and can be classified into three major classes: chemical, mechano-chemical and thermo-physical methods. For the mass productivity of metallic powder, the gas atomization would be an effective process but the obtained metallic powder has wide particle size range from nano-size to micro-size. The chemical methods are widely used to produce nanoparticles owing to the relative simplicity and the low energy consumption. However, the chemical methods also have a problem resulting in unwanted product during

* Corresponding author. Tel.: +82-32-850-0432; fax: +82-32-850-0410.
E-mail address: tkjung@kitech.re.kr.

1877-7058
Selection and peer-review under responsibility of ICM11 doi:10.1016/j.proeng.2011.04.121

chemical reaction. Quite recently, pulsed wire explosion method has been considered as an effective process to easily make metallic nanoparticles [1]. It allows several remarkable advantages which can easily make metallic nanoparticles, control particle size, and modify structures, and avoid unwanted product during chemical reaction, etc, [2-4]. It has been reported that the super heating factor (K) or the specific energy input into the wire (W/Ws) influence to particle size, morphology, and its structure in process using the pulsed wire explosion. The super heating factor depends on sublimation energy of metal wire, wire volume, and charging voltage. The super heating factor can be written as

$$K=W/Ws \quad (1)$$

$$Ws=V_{volume}\times w_s=\pi\times r^2\times l\times w_s \quad (2)$$

Here, Ws is the energy for sublimation of the wire, w_s is the sublimation energy of metal, r is radius of wire, l is wire length. It has been known that the productivity of nano particles increases with increasing the super heating factor. In recent years, many studies for metallic nanoparticles such as Al, Ag, Cu, Fe, W, and Ni using pulsed wire explosion method have been carried out [2-5]. Among the several metallic nanoparticles, Pt nanoparticles have been used for various applications, such as in catalyst fields for fuel cell batteries, CO_2 reforming, and reduction of harmful gases from automobile, etc [6-8]. Also, many researchers have tried to reduce the mass of Pt with keeping the efficiency because of high cost and limitation of natural resources. A reduction of the mass of Pt has been studied through a reduction of particle size or a mixing with other elements (composite). The composite nanoparticles have various structures such as solid solution type, precipitation type, satellite type and core-shell type, etc. These structures are mainly depended on the processing. For production of Pt based nanoparticles including composite nanoparticles, various studies including mechanical and chemical processes have been carried out. The fabrication of composite nanoparticles using pulsed wire explosion process can be achieved through wire explosion of clad wire. In this work, we carried out the pulsed wire explosion using Pt, Ni and Pt/Ni wires. Pt-Ni has mutual solubility. The aim of the work is to investigate morphology, size distribution and structure of Pt, Ni and Pt/Ni nanoparticles fabricated by pulsed wire explosion.

Experimental procedure

Pt, Ni and Pt/Ni wires were used for this experiment. Fig. 1 shows the SEM images for cross-sectional plane of wires used in this work. Pt/Ni wire was prepared by electro-less plating method. The volume fraction of Ni was approximately 30%. Wire explosion was carried out into water coolant. The detail experimental condition is presented in Table 1. Morphology, size distribution and structure of the produced powders were evaluated by TEM and XRD.

Table 1. Experimental conditions of wire explosion process.

Wire	*Diameter (mm)*	*Feeding length (mm)*	*Voltage (V)*	*Capacity (μF)*	*Sublimation energy of wire, w_s (J)*	*Super heating factor (K)*
Pt	0.1				58.4	5.22
Ni	0.1	40	320	2,200	53.9	5.66
Pt/Ni	0.12				variable	variable

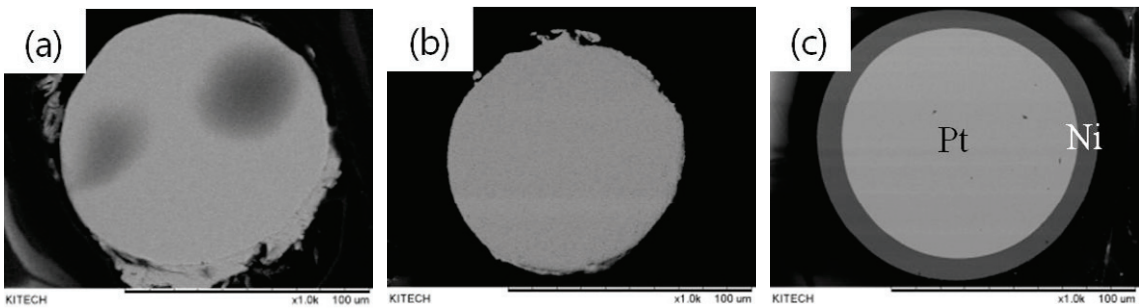

Fig. 1 (a) SEM images of Pt wire; (b) SEM image of Ni wire; (c) SEM image of Pt/Ni wire.

2. Results and discussion

Under the conditions of Table 1, most of wires were successfully exploded without unexploded pieces but it was found that the relatively larger powders were sunk to the bottom of the bottle. Using the powders except the powders sunk to the bottom, TEM study was carried out. Fig. 2 shows TEM micrographs of Pt, Ni and Pt/Ni nanoparticles produced in this experiment. It is found that the obtained nanoparticles are of spherical in shape and particle size of all powders lies in the range of a few nanometer up to ~100nm. No significant difference of particle shape and size between Pt, Ni and Pt/Ni nanoparticles wass seen. Generally, the particle size is strongly influenced by the applied super heating factor. In previous, we have reported that the mean particle size became smaller and size distribution became narrow with increasing the super heating factor using Ni wire. In this experiment, therefore, we set up the maximum applied super heating factor. Fig. 3 shows plots of size distribution analyzed from the TEM images of Pt, Ni and Pt/Ni nanoparticles. The obtained nanoparticles show the particle size ranges of a few nanometer to 60 nm for Pt nanoparticles and a few nanometer to 50 nm for Ni and Pt/Ni nanoparticles.

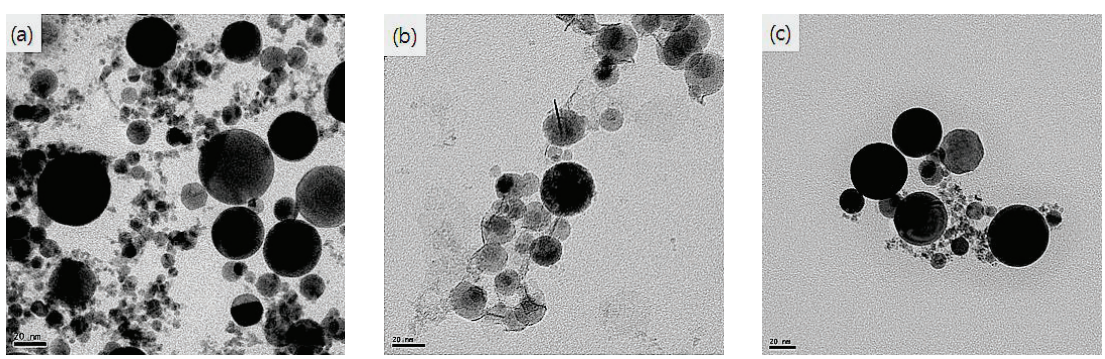

Fig. 2 (a) TEM micrographs of Pt nanoparticles; (b) TEM image of Ni nanoparticles; (c) TEM image of Pt/Ni nanoparticles.

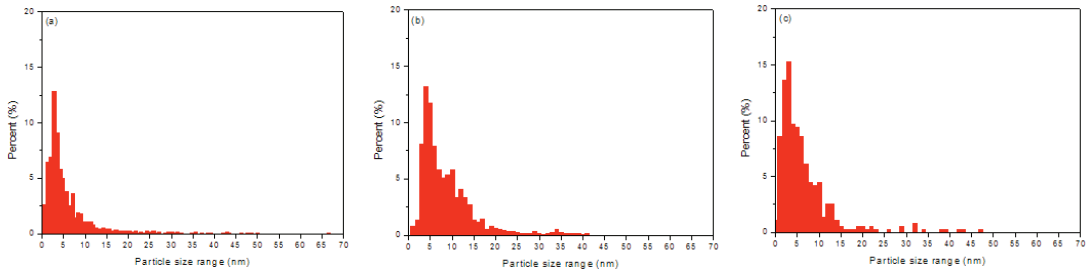

Fig. 3 (a) Particle size distribution of Pt nanoparticles; (b) particle size distribution of Ni nanoparticles; (c) particle size distribution of Pt/Ni nanoparticles.

When manufacturing metal nanoparticles using conventional processes, it is very difficult to suppress oxidation at surface of nanoparticles. Since the oxide layer results in a deterioration of desirable properties, additional step including chemical process would be needed to eliminate of oxide layer. In wire explosion process, it has been reported that the characteristics of passivated powders are strongly dependent on the production conditions and elements [9]. Fig. 4 shows high resolution TEM images and selected area diffraction patterns (SADP) of Pt and Ni nanoparticles. No oxide layer is seen in Pt nanoparticles and clear spot lines corresponding to Pt phase are observed, which indicates that the obtained Pt nanoparticles have high purity. This result indicates that the additional step to eliminate oxidation layer is not needed in wire explosion of Pt wire in D.I. water. Compared to Pt nanoparticles, Ni nanoparticles exhibited a partial surface exfoliation layer (crystalline) with 1 - 2 nm in thickness. Edward L. Dreizin has reported that the mismatching crystalline layer can be exfoliated from the main amorphous film (oxide layer) [9]. However, the oxide layer (amorphous) was well invisible at between the Ni crystalline and the exfoliation layer. Therefore, it is thought that these exfoliation layers and oxide layers are very partial and thin.

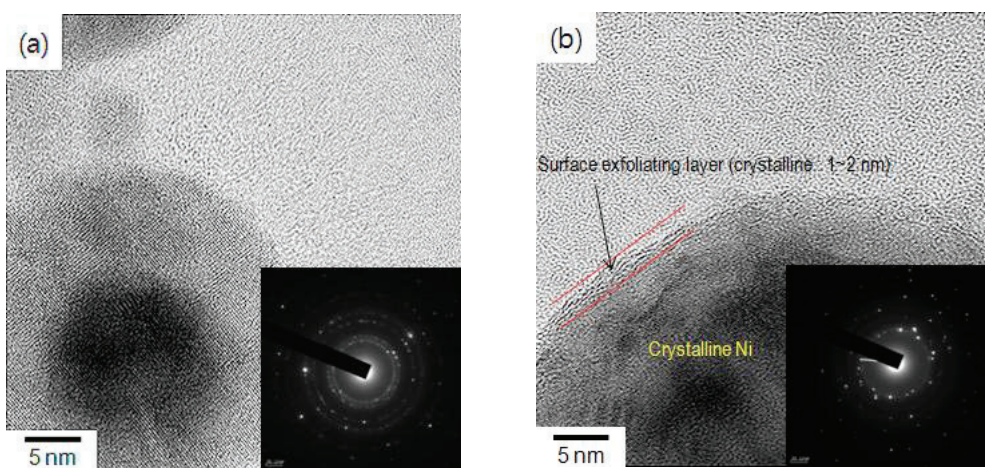

Fig. 4 (a) HR-TEM image and SADP of Pt nanoparticles; (b) HR-TEM image and SADP of Ni nanoparticles.

Fig. 5 shows HR-TEM image and TEM EDX-mapping result of Pt/Ni nanoparticles. No significant oxidation layer is observed. From EDX-mapping result, it is found that PtNi composite nanoparticles exist and their structures are solid solution type. Table 2 shows the TEM-EDX results for position 1 – 5 of Fig.5 (b). Basically, the contrast of nanoparticles can be varied not only by an atomic density but also by a particle size. From TEM-EDX results, the dark nanoparticles are Pt-rich phase but the concentration of Pt shows a slight difference for each nanoparticles. Compared to the dark nanoparticles (Pt-rich phase), the gray nanoparticles are Ni-rich phase. Therefore, it can be concluded that the pulsed wire explosion of Pt/Ni wire produces not only Pt-rich nanoparticles but also Ni-rich nanoparticles. Here, it should be noted that the gray nanoparticles are not necessarily Ni-rich phase because the high Pt concentration is detected even in some gray nanoparticles.

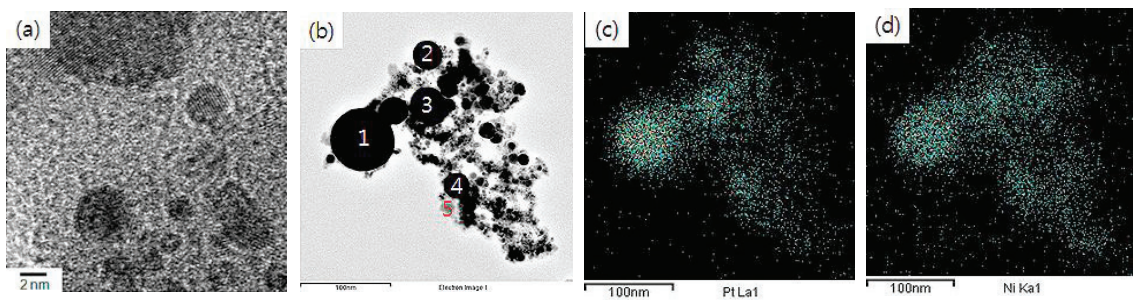

Fig. 5 (a) HR-TEM image of Pt/Ni nanoparticles; (b) TEM image of Pt/Ni nanoparticles; (c) TEM-EDX mapping result of Pt element; (d) TEM-EDX mapping result of Ni element.

Table 2. Chemical composition of the Pt/Ni nanoparticles.

Position	Pt		Ni	
	Weight %	Atomic %	Weight %	Atomic %
1	85.87	64.64	14.13	35.36
2	91.6	76.7	8.4	23.3
3	85	63	15	37
4	83.52	60.4	16.48	39.6
5	62.2	33.1	37.8	66.9

From TEM study, it is not easy to confirm that the Pt/Ni nanoparticles obtained by the pulsed wire explosion of Ni electroless plating Pt wire exclusively consist of PtNi composite nanoparticles. To investigate entire structure of the obtained nanoparticles, XRD study was carried out using Pt, Ni and Pt/Ni nanoparticles dried at 353K. Fig. 6 shows XRD profiles of Pt, Ni and Pt/Ni nanoparticles. In XRD profile of Pt nanoparticles, peaks corresponding to Pt are detected without additional peaks. On the other hand, in XRD pattern of Ni nanoparticles, peaks corresponding to Ni and NiO phase are simultaneously detected. These results are well consistent with TEM analysis result, although the oxide layer is very partial and thin. In XRD pattern of Pt/Ni nanoparticles, Pt, Ni, NiO and additional peaks are simultaneously detected. The additional peak is PtNi composite nanoparticles (Pt-solid solution). From TEM and XRD results, it can be concluded that the Pt/Ni nanoparticles obtained by the pulsed wire

explosion of Ni electroless plating Pt wire exclusively consist of Pt and Ni nanoparticles as well as PtNi composite nanoparticles.

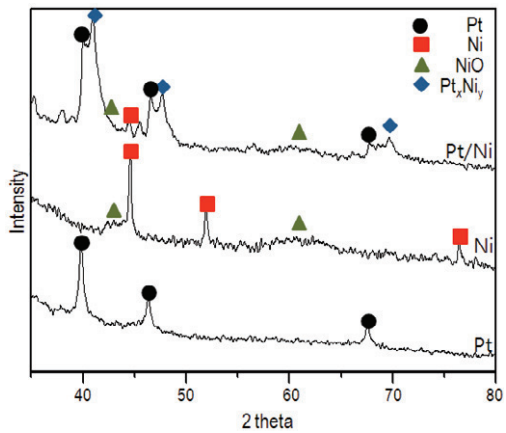

Fig. 6 XRD profiles of Pt, Ni and Pt/Ni nanoparticles.

3. Conclusion

Using pulsed wire explosion process in D.I water, Pt, Ni and Pt/Ni nanoparticles could be successfully obtained. The obtained nanoparticles were of sphere and showed the particle size ranges of a few nanometer to 50-60 nm. Unlike Pt nanoparticles, the partial and very thin NiO phase was found in the obtained Ni nanoparticles. It was confirmed that the obtained Pt/Ni nanoparticles consisted of Pt and Ni nanoparticles as well as PtNi composite nanoparticles of solid solution type.

Acknowledgment

This research was supported by a grant from the industrial Strategic Technology Development Program (Project No. 10037339) by the Ministry of Knowledge & Economy (MKE), Republic of Korea.

References

[1] Y.S. Kwon, A.P. Ilyin, D.V. Tikhonov, G.V. Yablunovsky, Materials Letter 62 (2008) 3143-3145.
[2] R.Sarathi, T.K. Sindhu, S.R. Chakravarthy, Materials Characterization 58 (2007) 148-155.
[3] B. Debalina, M. Kamaraj, B.S. Murthy, R. Sarathi, J of Alloys and Compounds 496 (2010) 122-128.
[4] Y.R. Uhm, J.H. Park, W.W. Kim, C.-H. Cho, C.K. Rhee, Materials Science and Engineering B 106 (2004) 224-227.
[5] C.H. Cho, S.H. Park, Y.W. Choi, B.G. Kim, Surface & Coatings Technology 201 (2007) 4847-4849.
[6] Long Q. Nguyen, Chris Salim, Hirofumi Hinode, Applied Catalysis A: General 347 (2008) 94-99.
[7] L. Gutierrez, E.A. Lombardo, J.O. Petunchi, Applied Catalysis A: General 194-195 (2000) 169-182.
[8] P.Forzatti, L. Lietti, N. Gabrielli, Applied Catalysis B: Environmental 99 (2010) 145-155.
[9] Y.S. Kwon et al, Applied Surface Science 211 (2003) 57-67.
[10] Edward L. Dreizin, Progress in Energy and Combustion Science 35 (2009) 141-167.